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A New Look at AP/Composite Propellant Combustion

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This article presents some theoretical studies on the time-independent and oscillatory combustion of nonmetallized ammonium perchlorate (AP)/composite propellants. The study has for its aim a coherent and unified interpretation of the voluminous data available from experiments related to propellant combustion. Three fundamental hypotheses are introduced: the extent of propellant degradation at the vaporization step has to be specified through a scientific criterion; the condensed-phase degradation reaction of ammonium perchlorate to a vaporizable state is the overall rate-limiting step; gas-phase combustion rate is controlled by the mixing rate of fuel and oxidizer vapors. In the treatment of oscillatory combustion, the assumption of quasi-steady fluctuations in the gas phase is used to supplement these hypotheses. This study successfully predicts several experimental observations including a few that were inconsistent with previous theoretical results.

Introduction

Despite extensive applications that solid propellant rockets find, a theoretical understanding of the fundamental combustion processes has eluded researchers. Consequently, the performance predictions depend almost totally on empirical information whose limitations are always clear. However, a thorough theoretical study must necessarily start at the fundamental level, and hence on extremely simple propellant formulations that are far removed from the state-of-the-art technology. This apparent absence of immediate applications has provided very little incentive for fundamental theoretical studies. The extremely complex nature of the problem itself has undoubtedly aggravated this situation to a large extent.

In the present work, a study is made of ammonium perchlorate (AP), nonmetallized composite propellants. The objective is to identify the fundamental processes that are likely to be common to a variety of propellants and propellant applications. The motivation for the present

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work comes from the observation that under normal conditions, the rate processes in the gas phase are likely to be much faster than those in the condensed phase. The present work differs from those available in the literature in three important aspects. The chemical kinetic degradation reactions in the condensed phase are explicitly included in the analytical treatment. The importance of a scientific criterion in specifying the extent of propellant degradation before vaporization is stressed, and it is shown that the usual arbitrariness is removed by applying the vapor pressure equilibrium criterion at the propellant surface. Lastly, the gas-phase chemical reactions are treated as wholly controlled by pressure-independent molecular mixing processes. It is found that the study predicts several of the features observed in AP/propellant combustion. Empiricism has been restricted to physical quantities whose values have been the subject of reasonable estimates in the past, and whose values should be within the grasp of experimental effort in the near future. The present work, which is best regarded as a feasibility study of research on a new path, has yielded very encouraging results in comparison with available experimental data. The same theory has, in addition, proved valuable in guiding and interpreting current experimental work (Ref. 1).

Physical Considerations

The fundamental physical structure of the present work is briefly discussed in this section.

It is of interest to know the mean molecular weight of the species leaving the propellant surface. This information is directly related to the extent of propellant degradation at the vaporization step, which, in turn, specifies the regression rate. In the combustion of AP/composites, the spectrum of possible species allowed by the chemical nature of the propellant is very rich. The mean molecular weight is an average over all of the species. However, by requiring that the species in the vapor phase, at the surface, be in vapor pressure equilibrium at the surface, the mean molecular weight may be determined (even without considering the chemical details of the species at the wall surface). After a study of American Petroleum Institute vapor pressure data (Ref. 2) on hydrocarbons, the following rule was evolved:

$$\mathcal{M} = \alpha P^{-\beta} \exp(\delta T_w) \tag{1}$$

If P is in atmospheres, and T_w in K, the constants have the following values (to slide rule accuracy): $\alpha = 32.8$, $\beta = 0.2615$, and $\delta = 3.67 \times 10^{-3}$. The approximate nature of the extrapolations of this rule to AP/polymers from hydrocarbon data is recognized; but it is felt that for a simple physical quantity like the vapor pressure, the chemical nature of the molecules is not critically important. As a matter of fact, the experimental vapor pressures of heptane (Ref. 2) and methylmethacrylate monomer (Ref. 3), which have the

same molecular weight of 100 g/g-mole, are very close over a range of temperature.

During the combustion of conventional AP/composite propellants, at a representative chamber pressure of 2×10^6 N/m^2, using the often-quoted value of 900 K for the wall temperature, we arrive (through Eq. 1) at a molecular weight of approximately 400 g/g-mole. This is much larger than the monomer molecular weights of most hydrocarbon fuel binders. If we consider AP deflagration alone, the value of 400 is not only much larger than the molecular weights of NH_3 and $HClO_4$ individually, it is much larger than the molecular weight of the (NH_4ClO_4) unit as well. Thus, it seems possible that microscopic fragments larger than a fuel monomer, or a (NH_4ClO_4) unit come off the surface. In polymer degradation studies, the presence of dimers, trimers, etc., has indeed been experimentally detected (Ref. 4). AP degradation studies have revealed the sublimation, as pure AP, under certain conditions. Even in experiments revealing the presence of NH_3 and $HClO_4$ species during the degradation of AP, it would seem logical to suppose that a crystal of AP (composed of many repeating units of NH_4ClO_4) would first degrade to smaller groups of NH_4ClO_4 before the final decomposition to NH_3 and $HClO_4$. In any attempt to experimentally determine the actual fragment size at the wall, it should be remembered that the entire process of propellant burning involves reacting species and that rapid quenching of all reactions is necessary, immediately after the species enter the vapor phase, to study the species leaving the surface. The mean fragment size of the species leaving the surface as a multiple of the fundamental repeating unit (in the condensed phase) will be designated the fragment size vaporizing, or simply *FSV*. The concept of *FSV* is a convenient (physically realistic) way of representing a more fundamental parameter in propellant combustion, namely the extent of degradation at the vaporization step. For a given backbone structure, the number of unbroken backbone bonds remaining in the fragments vaporizing is uniquely related to the *FSV*.

Now we consider the condensed phase reactions. In its unaffected state, AP (or the fuel) may be looked upon as a large "molecule" made up of the fundamental building blocks (NH_4ClO_4) (or the fuel monomer unit). Since the vapor pressure equilibrium criterion indicates that the *FSV* is approximately 2 to 10, under normally encountered chamber pressures, the question of the process by which the large "molecules" degrade into *FSV* arises naturally. As shown in Fig. 1, the propellant material in its travel from the deep solid region ($x \to \infty$) to the wall ($x = 0$) degrades from its unaffected (large molecular weight) state to vaporizable (small molecular weight) state. The reactions that bring about this degradation are therefore assumed to take place wholly within the condensed phase. Following the numerous studies on the degradation of AP (Ref. 5) and of polymeric fuels (Ref. 4), the degradation reactions are taken as first order Arrhenius reactions.

It is now necessary to consider the mechanistic details of the subsurface degradation of AP to relate the fundamental isothermal degradation rate of a homogeneous mass of AP to the degradation of macroscopic AP particles in

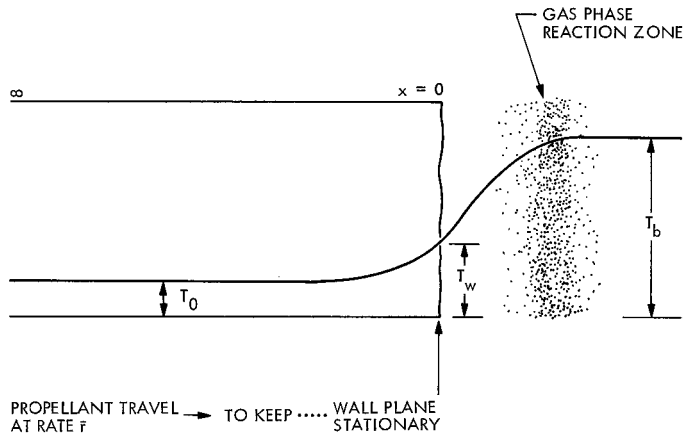

Fig. 1. General scheme of propellant combustion

the heterogeneous configuration in the propellant. The site of the active degradation of the AP particles in the solid is assumed to be a thin melt layer on the surface of AP particles. (It is to be clearly understood that such a model is put forward only as an "average" representation of the postulated physical phenomenon. The model is not to be interpreted too literally. If analogies help, it is suggested that the present model (shown in Fig. 2) be regarded in the same vein as the "plane" wall at the surface or the familiar flame "sheet", both of which are known to be inconsistent with physical reality, but nevertheless have proved extremely useful for analytical representation.) Assuming that the AP degradation is brought about by a reactive species that diffuses into the melt layer, the reaction rate is taken as directly proportional to the chamber pressure. Pressure-dependent degradation of AP has indeed been experimentally observed (Ref. 6), thus enhancing the credibility of the present model.

Next we consider the details of gas-phase processes in propellant burning. At atmospheric pressures the characteristic chemical kinetic time for air/hydrocarbon flames is of the order of 10^{-4} s. At much higher pressures, as in propellant burning, we expect the characteristic reaction times to be much smaller. The characteristic transport/mixing time (ratio of the combustion zone stand-off distance to the mean velocity of the vapors) in the burning of a composite propellant is of the order of 10^{-4} s. While these estimates are not conclusive, the general trend appears to be in favor of transport/mixing control and not of chemical kinetic control of the gas phase rate-limiting process. (It is to be remembered that the oxidizers used in propellant are much more powerful than air). In any case even the mixing time of 10^{-4} s is much too small in comparison with the typical time scale in the *condensed phase* (10^{-3} s). Thus the *overall* rate-limiting reactions in propellant burning are very likely to be in the condensed phase. Such a belief is consistent with the general feeling that among the three zones of interest to propellant

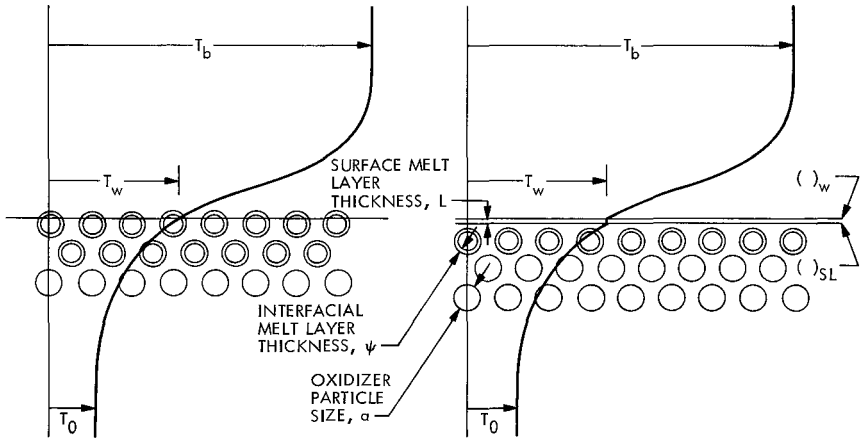

Fig. 2. Details of the postulated model for composite propellant combustion: (a) subsurface reactions only; (b) surface reactions in a melt layer augmenting subsurface reactions

combustion (high temperature vapor-phase, medium temperature gas/solid interface, and low temperature condensed phase) the processes in the condensed phase are probably the slowest.

The reactants burn in a nonpremixed combustion zone in the vapor phase except in the following two cases:

(1) Gas phase chemical-kinetic rates become very low because of very low pressures or special ingredients, so that molecular mixing processes take the gases to a premixed state before combustion.

(2) A thorough mixing of fuel and oxidizer takes place in a surface layer on the propellant before they enter a vapor phase.

It is seen in what follows that the simplest model of the gas phase combustion zone (treated like a "black box") is adequate for our purposes.

Numerical Values of Constants

The following values have been consistently used throughout this work (Ref. 7 has the explanation):

(1) Thermal diffusivity:

Pure polymer base	10^{-3} cm²/s
Normal AP composites with heavy AP loading	1.1×10^{-3} cm²/s
Pure AP	1.5×10^{-3} cm²/s

(2) Fundamental rate data on pure AP (Ref. 5, p. 41):

$$B = 9.2 \times 10^7 \text{ s}^{-1}$$

$$E = 121.1 \times 10^3 \text{ J/mole}$$

(3) Heat of degradation D [Ref. 8]:

$$D = 2{,}450 \text{ J/g}$$

The remaining task is essentially mathematical analyses, along with the treatments of some details that arise naturally. The analyses are not presented in this article due to limitations of space. (They are available in Ref. 7.) Since a majority of AP composites are heavily loaded (≈80%) with ammonium perchlorate, the behavior of AP by itself is pursued in some detail in the following section. The time-independent combustion of composite propellants, and the oscillatory combustion of composite propellants are treated separately; the concluding remarks complete this article.

Degradation and Deflagration of Ammonium Perchlorate

The aim of this section is the theoretical prediction of the linear regression rate of AP as a function of chamber pressure (or other experimentally determined conditions). In the coordinate system used (Fig. 1), the wall surface is held stationary. We follow the changes in a plane (dx) as it moves up with time from deep solid ($x = \infty$) to the wall ($x = 0$). The temperature of the layer increases from the deep solid value (T_0) to the wall temperature (T_w); the mean fragment size of the AP changes from a very large value (approaching "infinity" for practical purposes) at T_0, to FSV at the wall, $(\ )_w$.

Following the numerous studies in the field, the degradation of AP is modeled as a first-order Arrhenius reaction. The pre-exponential factor is taken as directly proportional to the pressure in the molten state (discussed later), and independent of pressure in the solid. The cases of subsurface reactions only and surface reactions augmenting subsurface reactions are treated separately.

Although we are interested at present in the steady state only, the full (time-dependent) equations are written down since these are needed later in the analysis of oscillatory burning.

Energy:

$$k\frac{\partial^2 T}{\partial x^2} + c\rho r\frac{\partial T}{\partial x} - \rho c\frac{\partial T}{\partial t} = D\rho NB \exp(-E/\mathcal{R}T) \tag{2}$$

Bond Conservation:

$$-\frac{dN}{dt} = NB \exp(-E/\mathcal{R}T) \tag{3}$$

Boundary Conditions:

$$\left.\begin{array}{llll} x = 0: & T = T_w; & x = \infty: & T = T_0 \\ x = 0: & N = N_w = 1 - \dfrac{1}{FSV}; & x = \infty: & N = 1 \end{array}\right\} \tag{4}$$

The regression rate eigenvalue (r) is thus determined by a solution of the above nonlinear system of equations. The activation energy E has a value like 125×10^3 J/mole, while the maximum temperature (which is at the wall) is like 900 to 1000 K. Hence, $E/\mathcal{R}T$ is at least 10 to 15. This implies that the right hand sides of Eqs. (2) and (3) assume exponentially small values even at short distances from the wall. Such a behavior is particularly suited for a matched asymptotic analysis (Ref. 7), the final result from which is

$$r = \left[\frac{(k/\rho c)\, B \exp\left(-E/\mathcal{R}T_w\right)}{(E/\mathcal{R}T_w)\left(\dfrac{T_w - T_0}{T_w}\right)\left[\left\{\dfrac{D}{c\,(T_w - T_0)} + 1\right\} \ln\left(\dfrac{FSV}{FSV - 1}\right) - \dfrac{D}{c\,(T_w - T_0)\,FSV}\right]}\right]^{1/2} \tag{5}$$

Recalling that the above result does not include surface (heterogeneous) reactions, we should compare the results from experiments where there is little possibility of such surface reactions. The familiar hot-plate experiments come under this category. However there are indications that a criterion other than the vapor pressure equilibrium criterion is needed to specify the fragment size at the wall, because there exists no clearly-defined equilibrium interface between a condensed-phase and a vapor-phase. A mechanical strength criterion seems more appropriate. That is, as the material degrades from deep within the solid, a plane is reached where the increasing temperature and decreasing physical strength force the material out of the surface. It was seen (Ref. 9) that a constant molecular weight of 900 appears to match experimental data very well for the polymer PMMA in such hot-plate experiments. A molecular weight like 900 corresponds to an FSV value like 7 to 8 for AP (fundamental molecular weight of $NH_4\,ClO_4$ is 117.5 g/g-mole), and a value of 8 is used in the present study. At these high values of FSV, 7 or 8 will not make more than about 7% difference in the final regression rate (Eq. 5), an error that is much smaller than the general levels of uncertainty in such experiments.

Presented in Fig. 3 are the experimental data points collected by Powling (Ref. 10) from many different sources. The theoretical prediction (Eq. 5) is also plotted. Good agreement is evident. It is noted that because of the square root factor in Eq. (5), an overall activation energy of nearly 62.5×10^3 J/mole would be inferred by forcing an Arrhenius expression through the hot-plate data points. Actually, such curve fit procedures grossly average the fundamental processes. The valid procedure is to use the isothermal Arrhenius parameters (obtained from experiments on very small samples of AP) in Eq. (5), as has been done here.

While the hot-plate data support the model, several inconsistencies arise when an attempt is made to generalize the above model to self-deflagration

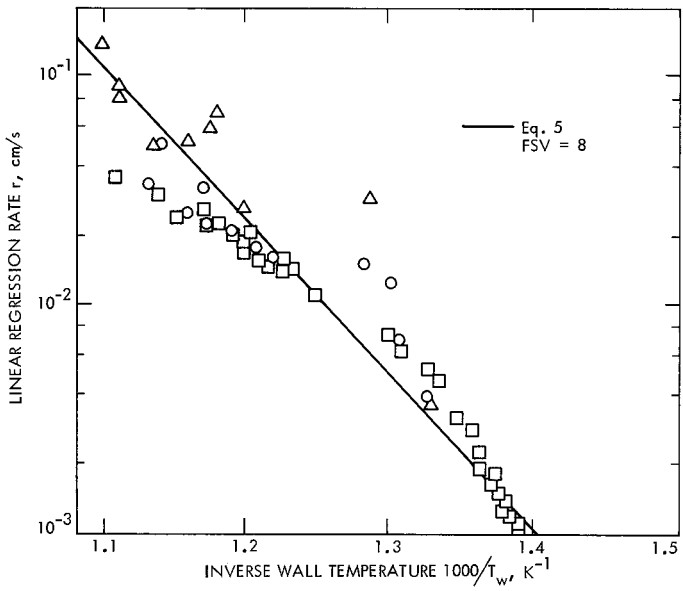

Fig. 3. Theoretical predictions for AP, and comparisons with the hot-plate data from Powling (Ref. 10)

flame-heated AP. The disagreements noted in Ref. 7 lead us to the following picture.

Since pressure dependence is an important aspect of self-deflagration, and since pressure-dependent reactions are difficult to visualize in the solid state, let us make the simple postulate that *surface degradation in a melt layer aids subsurface thermal degradation in producing vaporizable fragments and that at high pressures it completely overwhelms the subsurface contribution.* The experimental observation of a "liquid" layer on the surface of deflagrating AP (Ref. 11) lends credence to such a picture.

With the above physical picture, the value of the linear regression rate is given by the equation,

$$r = \frac{\text{Fundamental degradation rate in the melt layer of thickness } \ell}{\text{The number of bonds to be broken}} \qquad (6)$$

With the scheme of a first-order reaction, the degradation rate of the mass of AP in the melt layer depends on the extent of degradation in the melt layer, which is represented by the mean fragment size of AP in the melt layer. Consistent with the experimental evidence (Ref. 5) of considerable activity in the melt layer, a uniformly mixed layer is assumed. The arithmetic mean fragment size is used for the AP fragments in the melt layer. However, the fragment size *at the vaporization step* is specified by

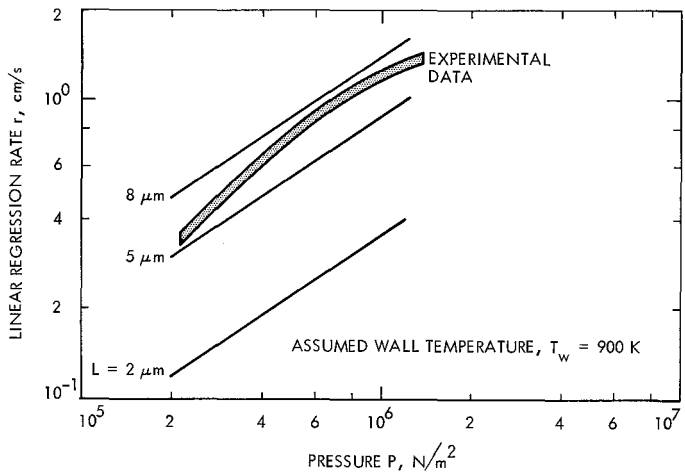

Fig. 4. Linear regression rate of self-deflagration flame heated AP and comparison with experimental data (Ref. 11)

the vapor pressure equilibrium rule. It is shown (Ref. 7) that the linear regression rate can be written,

$$r = \ell\,(FSV - 1/2)\,B_0\,(P/P_0)\exp(-E/\mathcal{R}T_w) \tag{7}$$

Predictions through Eq. (7) are compared with experimental data (Fig. 4) for three assumed values of the melt layer thickness ℓ. A constant value of the melt layer thickness (between 5 μm and 8 μm) is seen to match the experimental data quantitatively. However, since the melt layer thickness ℓ decreases with increasing regression rate (increasing pressure) as shown in Ref. 7, this agreement should be due to self-compensating effects of slight increase in wall temperature with pressure (Ref. 12) and the decrease in the melt layer thickness.

To explore the effects of initial temperature, it is noted that Eq. (5) is applicable for the solid phase below the melt layer; however, the fragment size at the solid-liquid interface (called *FSSL*) has to be used in place of *FSV*. Equation (5) predicts the dependence on initial temperature T_0 as

$$r \propto 1/[(T_w - T_0)/T_w]^{1/2}$$

The $\ell = 5$ μm curve in Fig. 4 is plotted in Fig. 5 for three different values of T_0. The experimental data of Ref. 13 are also presented.

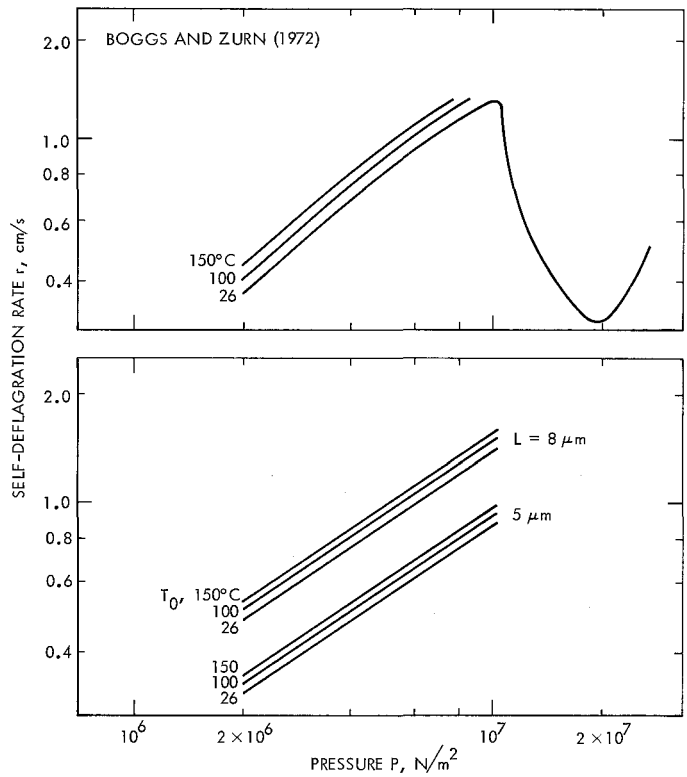

Fig. 5. Linear regression rate of self-deflagration flame heated AP and comparison with experimental data (Ref. 13) on initial temperature sensitivity

A striking feature of single crystal AP self-deflagration experiments is the abrupt dip in the regression rate that is observed around 1.38×10^7 N/m^2. The thickness of the melt layer used in this treatment is observed to (Ref. 5), and can be theoretically shown to (Ref. 7), decrease with increasing regression rates at a constant wall temperature. Finally, at a high enough regression rate, the melt layer may occupy only a very small portion of the surface. (In the ideal one dimensional picture, the melt layer disappears completely.) When this happens, the degradation by the reactive species becomes very slow because mobility through the solid is *much* slower than through a liquid. The process of degradation is now more likely to be controlled completely by subsurface thermal degradation. A marked drop in the regression rate may be expected after such a point is reached. An exploratory calculation has indicated that the sudden dip observed experimentally (around 1.38×10^7 N/m^2) may indeed be due to such a phenomenon.

Time-Independent Combustion of Composite Propellants

The hypotheses and principal conclusions from the previous sections are applied to the problem of composite propellant burning. We continue to consider only those cases in which chemical kinetic rates of combustion reactions in the gas phase are far greater than transport and mixing rates; the overall rate controlling reactions (viz., fundamental degradation of AP) occur in the condensed phase. The concept of *FSV* is generalized to include multicomponent vapor phase/condensed phase equilibrium. It is required to include the degradation kinetics of the binder as well. The influence of burning rate catalysts is examined in the light of the same model used for uncatalyzed propellants; the increased reaction rate in a surface layer accounts for the increased regression rate. The effect of the oxidizer particle size is studied in the simplest manner. In the condensed phase, its effect is introduced as variations in the surface area for the degradation of AP. The regression rate is predicted (by a slightly modified version of Eq. 5) as a function of the chamber pressure and the wall temperature. The case of the subsurface reactions only, and the case of surface reactions augmenting subsurface reactions are treated separately.

To render the system self-determined, it is required to specify the wall temperature through gas-phase energetics and fluid mechanics. For this purpose, the familiar one-dimensional gas phase model is invoked. In the absence of a satisfactory theory for the gas phase details, the two limiting cases considered here both lead to results sufficiently close to reality.

Rate-Controlling Reactions in the Subsurface Region

We start with the assumption that *the rate-controlling reactions (AP degradation) occur in a thin layer on the surface of AP crystals in the solid.* The propellant material is represented as homogeneous for the purposes of heat transfer calculations. The process of heat conduction is assumed to be adequately represented by Fourier's law with a properly averaged material property of thermal conductivity. It is necessary to have the above picture clearly understood to prevent the extrapolations of the results beyond their limits of validity. For example, the homogeneous solid assumption does not appear to be valid when the characteristic thermal depth in the solid (κ/r) becomes far less than the oxidizer particle size (a). That is, at high regression rates (and hence at high pressures) the results need careful interpretation.

When we consider the differential element dx in the analysis, and write the reaction rate in that element, we have to properly consider the actual volume in the differential element in which the degradation reactions are taking place. As a first approximation, a unimodal distribution of spherical AP particles is assumed. If the reactions take place in a layer of thickness ψ on the surface of AP particles, the volume of AP undergoing degradation reactions per particle is very nearly equal to $\pi a^2\psi$, where a is the diameter of the AP particles. The physical volume of the AP particle is $\pi a^3/6$. If v is the volume fraction of AP loading in the propellant, the volume fraction

undergoing degradation is $(6\psi v/a)$, so that the reaction rate in the layer of thickness dx is multiplied by this factor. The rest of the analysis is identical with that for a homogeneous solid. Hence, we substitute the above factor into Eq. 5 and obtain:

$$r = \left\{\left(\frac{6\psi v}{a}\right)\frac{(k/\rho c)\,(B_0 P)\exp\left(-E/\mathcal{R}T_w\right)}{(E/\mathcal{R}T_w)\left(\dfrac{T_w - T_0}{T_w}\right)\left[\left\{\dfrac{D}{c\,(T_w - T_0)} + 1\right\}\ln\left(\dfrac{FSV}{FSV - 1}\right) - \dfrac{D}{c\,(T_w - T_0)\,FSV}\right]}\right\}^{1/2} \tag{8}$$

It is carefully noted that the value of $(k/\rho c)$ is that of the propellant and *not* of AP alone. The value of ψ is left as a parameter. For specifying the FSV through the vapor pressure equilibrium criterion, the statistical mean fragment size has to include averaging over the binder species also. The assumption of a plane regressing wall requires that the regression rate of the binder in the propellant has to equal the regression rate of the AP in the propellant. The regression rate of the binder is predicted by Eq. (5) if the thermochemical constants used in Eq. (5) are those of the binder material. For a typical binder (CTPB) and typical numerical values of the composite propellant characteristics, the predictions are presented in Fig. 6.

Joint Rate Control by Subsurface and Surface Reactions

The assumption of subsurface reactions alone is insufficient to account for all of the experimental observations. It is suggested that under certain circumstances surface reactions in a thin layer augment subsurface reactions. After the material reaches the plane SL (Fig. 2b) in its travel from the deep solid region (∞) to the surface, the binder and the oxidizer mix thoroughly in a melt layer of thickness L. This well stirred layer is assumed to be isothermal. In the case of catalyzed propellants, the catalyst is taken as inactive in the subsurface region (below the plane SL) and active in the surface layer. (The catalyst, for its action, has to mix well with the propellant on the microscopic level, a process that is difficult to visualize in the solid, but seems natural in the melt layer.) The regression rate eigenvalue determined by the subsurface reactions has to equal the regression rate determined by the surface reactions. The numerical solution for a typical case is presented in Fig. 7. The curves of regression rate versus pressure with L as a parameter may be considered the same as curves with the surface degradation rate as a parameter (possibly through catalysis), since the ultimate effect of either of the two is felt the same way in the regression rate. Since it is known that the melt layer thickness decreases with increasing regression rate, the regression rate versus pressure curve is likely to have the shape shown by the broken line in Fig. 7. Propellants with binders that *melt readily* have indeed been known (Ref. 14) to exhibit such a decreasing n behavior.

Gas Phase Details

In the combustion of propellants the wall temperature is determined by the interaction of the solid phase with general fluid dynamics and energetics

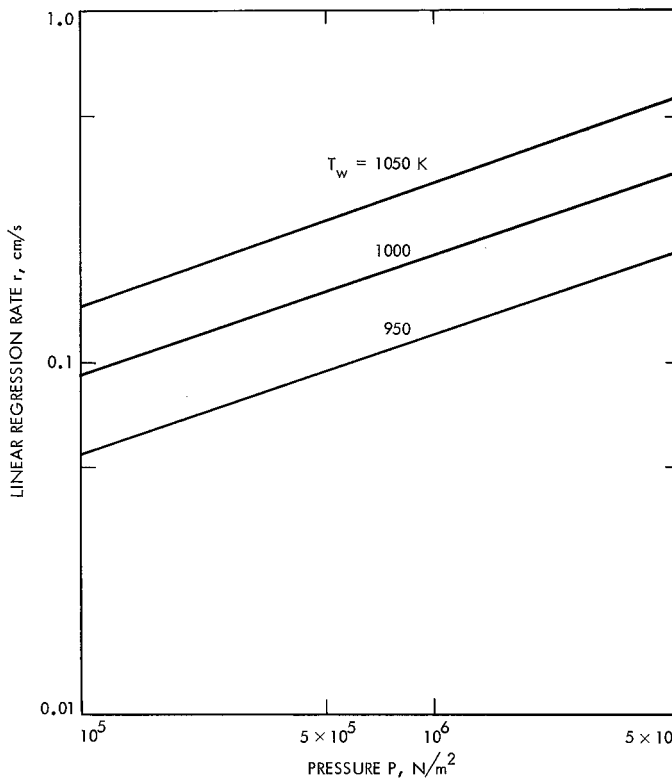

Fig. 6. Theoretical predictions for a typical composite propellant considering subsurface reactions only (mass fractions: 0.75 AP, 0.25 CTPB; AP particle size, a = 90 μm, interfacial reaction layer thickness, ψ = 5 μm)

of the gas phase. The detailed solution depends on the assumptions we make regarding mixing and combustion.

It is difficult to characterize the gas phase above the burning composite as either laminar or turbulent. For double base propellants (*and* for composites having extremely fine oxidizer particles) there appears to be little room for doubt regarding the existence of laminar flow, simply from Reynolds number considerations. For normal composite propellants, photographs of the combustion zone reveal that the gas phase is far from being laminar. There are present "spots" that give rise to transport and mixing on a scale far larger than molecular. However, the flow field may not merit the use of the word "turbulent" in that the origin of the large-scale spottiness has little to do with classical Tollmien-Schlichting instability. Moreover, and this is an important consideration, it is difficult to conceive of an exchange mechanism that would establish the standard turbulent energy spectrum that incorporates proven features such as, for example, Kolmogorov and Heisenberg limits. These thoughts render inapplicable a host of useful empirical rules that fluid dynamicists have evolved on flows that are truly turbulent. The

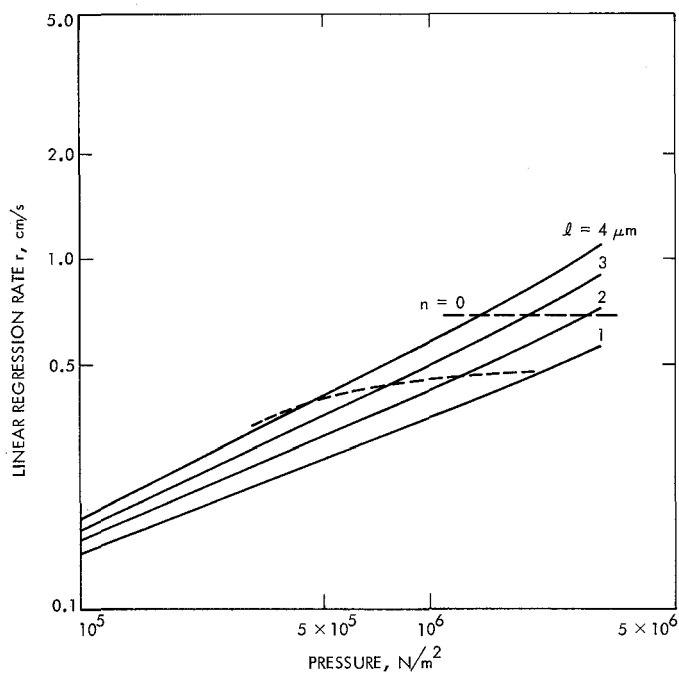

Fig. 7. Theoretical predictions for a typical AP composite propellant. Surface reactions in a melt layer (of thickness ℓ) augementing subsurface reactions

point to note is that we can not assume the flow to be *turbulent* simply because it is *not laminar.*

Two limiting cases are considered for the treatment of the gas phase here.

Case 1: The familiar flame-sheet approximation; no combustion until the gases have traversed a distance x^* from the surface, and complete combustion in a negligible distance after x^*.

Case 2: Uniform combustion at a constant rate $\dot{m}'''$ (g/cm^3-s) starting from the solid-gas interface plane $(\ )_w$.

Case 2, above, is recognized as the familiar concept of "well stirred reactor". Since the combustion rate is controlled by the molecular mixing processes, the gravimetric reaction rate may be taken as directly proportional to the density of the gases. Since, in the range of normal interest, the combustion temperature does not vary appreciably with mean pressure, it is seen through the state equation that the reaction rate $\dot{m}'''$ is directly proportional to the pressure (that is, $\dot{m}''' = A \cdot P$, where A is a constant).

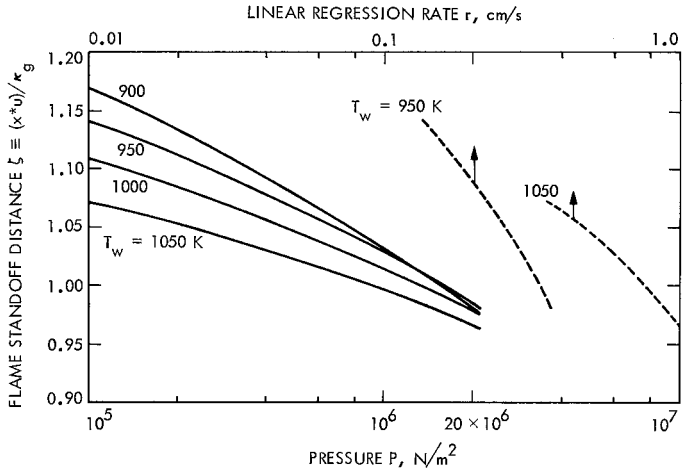

Fig. 8. Variations in flame standoff distance for a typical composite propellant within the flame sheet approximation (flame temperature T_b = 2750 K)

A solution to the energy equation applied between the wall plane $(\ )_w$ and the flame sheet $(\ )_b$, using the matching condition that the heat flux into the solid has to match the heat balance at the wall, yields the details of flame standoff distance (x^*) variations with pressure, with the wall temperature as a parameter. The results are presented in Fig. 8 for a typical case.

For the other case of uniform combustion, the solution requires the value of the reaction rate $\dot{m}'''$ which has been taken from Ref. 7. The solutions to the one-dimensional energy equation are presented in Figs. 9 and 10 and show the linear regression rate (r), wall temperature (T_w) and the distance of the plane of complete combustion (analogous to the earlier x^*) for a typical propellant for assumed values of the various parameters. In comparison with predictions based on the assumption of constant wall temperature/flame sheet, the general behavior is not appreciably different quantitatively or even qualitatively. It would appear that the actual model employed for the gas phase processes is not crucially important in determining the general trends so long as the overall rate controlling reactions occur in the condensed phase. Such a conclusion was anticipated earlier purely on physical grounds.

Oscillatory Burning of Composite Propellants

The role of the propellant in pressure-coupled instability is thought, at the present time, to be well represented by the response function, defined as

$$\mathcal{R} \equiv \frac{\tilde{\mu}}{\tilde{\epsilon}} = \frac{r'}{\bar{r}} \cdot \frac{\bar{P}}{P'}$$

with the familiar nomenclature. On the theoretical side, the numerous derivations of the response function have been shown to be essentially identical (Ref. 16), since the fundamental assumptions in the various analyses are identical. On the experimental side doubts exist regarding proper processing of the measured variables to yield the real part of the response function. Nevertheless, some of the general trends in the experimental response functions are thought to be well understood. (That is, comparisons of theory with experiments *are* meaningful.) The response function is usually found to be dependent upon the mean pressure, contrary to theoretical predictions. There exist experimental data that show very large values for the response function at low frequencies, while theoretical predictions suggest that the response function must tend to the limit of the steady-state pressure index (n), in the limit as frequency tends to zero.

In this section the response functions for model composite propellants are derived considering the two cases of subsurface reactions only, and surface reactions in a melt layer augmenting subsurface reactions; the gas phase fluctuations are modeled under the two cases of adiabatic processes and uniform combustion. These theoretical predictions are found to be consistent with several experimentally observed features including the mean-pressure dependence.

Subsurface Reactions with No Surface Reactions

The temperature change across the reaction zone is of the order of reciprocal activation energy parameter (i.e., $1/\theta_a$, with $\theta_a \equiv E/\mathcal{R}T_w$). This reaction zone has a physical thickness $\sim \kappa/\bar{r}\,\theta_a$. Thus, so long as we restrict our attention to small amplitude ($\sim 1/\theta_a$) fluctuations, the effect of the mean temperature variation across the reaction zone is a second order quantity that need not be included in a first order analysis. That is, if we visualize a (hypothetical) freezing layer below which chemical reaction rates are negligible compared to other processes, we can neglect the effects of the mean temperature variations between the wall and the freezing layer on fluctuations of temperature. Also, phase differences in variables may be neglected across the reaction zone except at very high frequencies. This fact can be exploited to write the exact expression for the wall boundary condition. We first use a coordinate frame of reference held fixed at the mean position of the fluctuating wall (or the freezing layer). We obtain the outer solution, neglecting the reaction term. This exact solution is then used to write the temperature-gradient boundary conditions both at the freezing layer (the interface between the "inner" and the "outer" regions) and on the

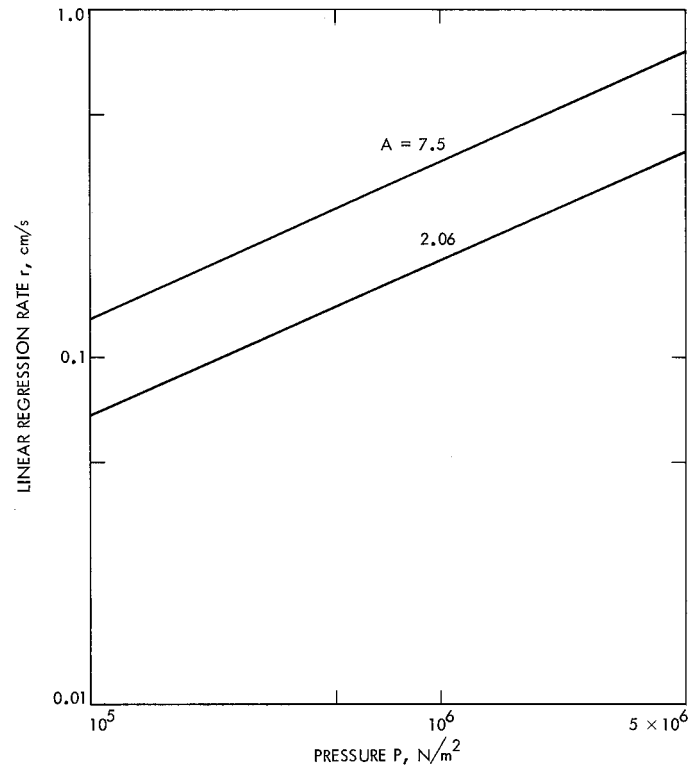

Fig. 9. Theoretical predictions for a typical composite propellant considering subsurface reactions only. The assumption of uniform combustion in the gas phase ($\dot{m}''' = AP$)

wall. Then we solve for the time-dependent regression rate in a manner analogous to the time-independent case. That is, we solve the full equation, including explicitly the Arrhenius reaction rate term in the "inner" region.

The analysis is then generalized to include the case of surface reactions augmenting the subsurface reactions.

After considerable algebra, detailed fully in Ref. 7, the response functions derived on the basis of condensed phase analyses are written.

$$\mathcal{R} \equiv \frac{\left(\frac{r'}{\bar{r}}\right)}{\left(\frac{P'}{\bar{P}}\right)} = \text{fn}\left[\Omega, \lambda, \bar{\theta}_a, \frac{\tau'_w}{\left(\frac{r'}{\bar{r}}\right)}, R_i\right]$$

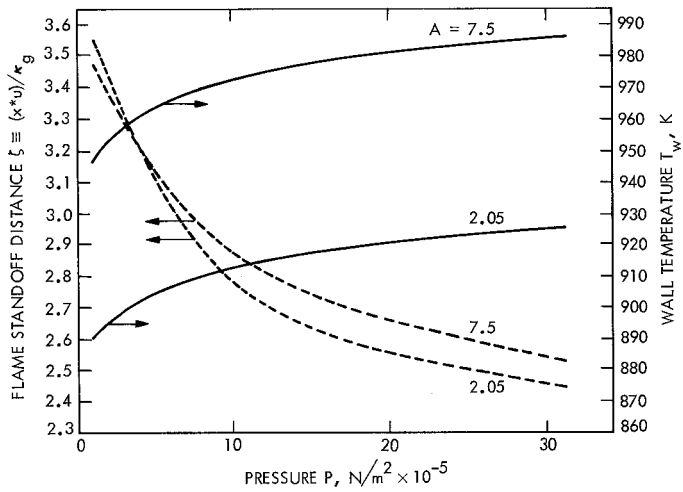

Fig. 10. Variations in flame standoff distance and wall temperature for a typical composite propellant within the uniform combustion approximation

where

Ω is the normalized frequency ($\equiv \omega\kappa/\bar{r}^2$)

λ is the normalized mean regression rate

$\bar{\theta}_a$ is the reduced activation energy parameter ($E/\mathcal{R}\bar{T}_w$)

τ_w' is the normalized amplitude of wall temperature fluctuations

R_i are constants dependent, for most part, on steady-state parameters in propellant burning.

The analysis of condensed phase details alone leaves the variable τ_w' to be specified from an analysis of the gas phase details. The same two models (flame sheet approximation and uniform combustion) used in time-independent combustion are used in the oscillatory case along with the assumption of adiabatic fluctuations at the flame sheet in the former model.

Surface Reactions Augmenting Subsurface Reactions

Considering the condensed phase details only, the case of surface reactions augmenting subsurface reactions is very similar to that of steady-state combustion (Fig. 2b). The only difference from the steady burning case is that the *fluctuating* part of the regression rates in the subsurface region and the surface melt layer need not be equal to each other, as the *steady* part of the regression rate has to be. The difference between the fluctuating

parts of the regression rate in the surface and subsurface regions shows up as fluctuations in the thickness of the melt layer. In the time-independent combustion of composite propellants, the surface melt layer thickness (L) during time-independent combustion was supplied from considerations external to the condensed phase analysis. In the oscillatory case here we consider two limiting conditions: (1) the melt layer thickness is constant even during unsteady combustion, (2) the subsurface regression rate fluctuation vanishes and hence, all the fluctuation in the regression rate is entirely due to the fluctuating melt layer.

As shown in Fig. 11, six response functions are possible for the six models postulated here; all six of them are derived in Ref. 7. At the time of the present article, some of the details pertaining to the case of adiabatic fluctuations in the gas phase, with subsurface reactions only, are being carefully scrutinized and are not presented here. Three of the other five response functions are presented in Figs. 12, 13, and 14. The model propellants considered here are the same ones for which steady combustion rates were presented earlier.

A distinct feature of the present response functions is that they exhibit dependence on mean chamber pressure. As explained earlier, the pressure dependence during time-independent combustion arises from two independent processes: pressure-dependent degradation reactions, and the vapor pressure equilibrium effect. Due to phase differences among the various fluctuating quantities, it is possible for these two effects to be differently affected during oscillatory combustion as compared to time-independent combustion. The dependence on mean chamber pressure of the derived response functions is due to such an effect. For the special case of a zero-n propellant, strong oscillatory combustion is possible again for the same reason.

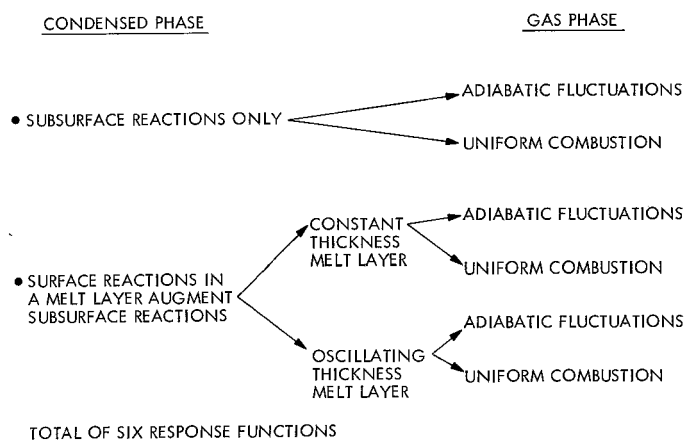

Fig. 11. General scheme of response function derivations in the present study

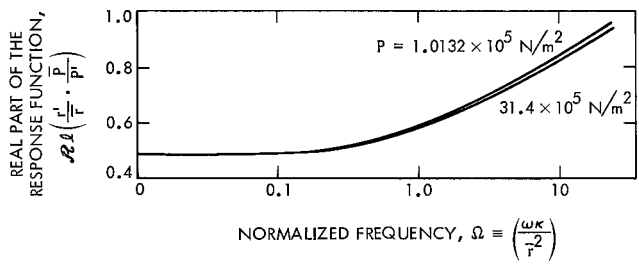

Fig. 12. Typical theoretical response functions of the present study, Example 1: subsurface reactions with no surface reactions, uniform combustion in the gas phase

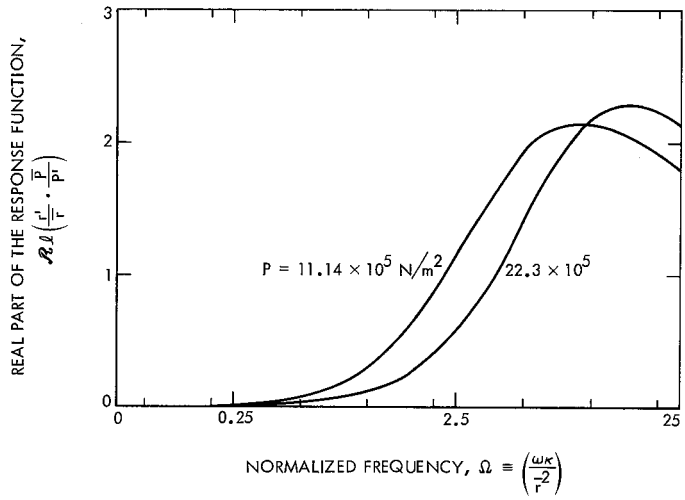

Fig. 13. Typical theoretical response functions of the present study, Example 2: surface reactions in a melt layer of fluctuating thickness, fluctuating part of regression rate due to subsurface reactions zero, adiabatic fluctuations in the gas phase

Two features of the present calculation are worth repetition. Simplifications were introduced by limiting our attention to moderate frequencies, so that the interpretation of the theoretical results above a nondimensional frequency (Ω) of 10 is questionable. Secondly, for the purposes of heat transfer calculations, the assumption of a homogeneous solid was made. That is, the assumption of the characteristic linear dimension (effective thermal

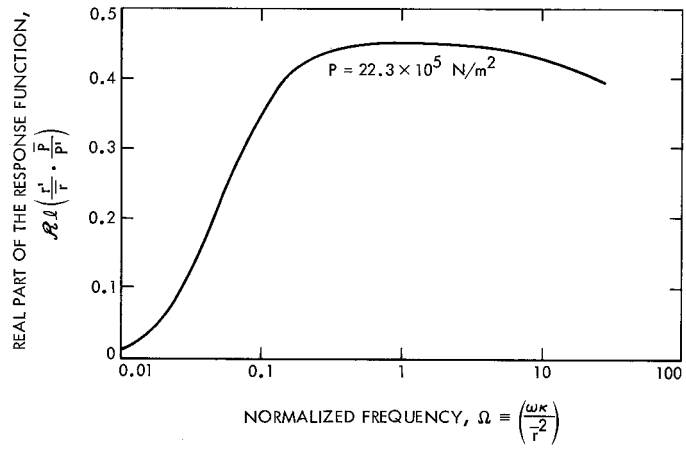

Fig. 14. Typical theoretical response functions of the present study, Example 3: a propellant having n = 0; uniform combustion in the gas phase

depth, $\sim\kappa/\bar{r}$) associated with the heat transfer process in the solid being far larger than the characteristic linear scale (oxidizer particle size, a) associated with solid heterogeneity is inherent in all of the present derivations. Since the thermal diffusivity (κ) may be taken as constant during the small variations, if any, in the wall temperature, the assumption of a homogeneous solid becomes questionable at high regression rates and hence at high pressures. This is an important consideration amply appreciated during the current experimental studies at JPL.

Examining reported experimental data on the response functions of composite propellants (Refs. 15 and 17), we note several similarities with the present theoretical predictions.

Conclusions

The present work on the combustion of AP/composite propellants leads to the following conclusions.

(1) The assumption of condensed-phase degradation of AP being the rate-limiting step in the overall pyrolysis of AP leads to theoretical results that match well with experimental hot-plate data.

(2) The hypothesis of pressure-dependent (condensed phase) degradation of AP in a surface layer controlling the overall regression rates of AP/composite propellants leads to predictions in agreement with experimental data covering both single-crystal AP self-deflagration and composite propellant combustion.

(3) The extent of degradation at the vaporization step can be specified through the vapor pressure equilibrium criterion.

(4) The hypothesis of gas-phase combustion rate completely determined by pressure-independent diffusive-mixing processes leads to analytical results in agreement with experimental trends.

(5) The response function of a composite propellant can be theoretically derived through the method of "inner" and "outer" expansions including explicitly the nonlinear (Arrhenius) degradation rate term in the condensed phase.

(6) The response functions so derived exhibit dependence on mean pressure, strongly so with the model of adiabatic fluctuations and weakly with the model of uniform combustion in the gas phase.

(7) A "zero-n" propellant *can* exhibit fairly strong instability behavior.

(8) A few unifying concepts enable us to coherently interpret a host of superficially diverse data.

The gas phase processes in composite propellant combustion form the darkest area in the field, and further research is badly needed to illuminate this important facet.

Nomenclature

A constant in the uniform combustion law, g-cm^{-3}-s^{-1} (10^5 N/m^2)$^{-1}$

a mean size of the oxidizer particles in the composite propellant, cm

B pre-exponential factor in the Arrhenius law for thermal degradation, s^{-1}

c specific heat, J-g^{-1}-°C^{-1}

D heat of degradation of the solid, i.e., heat required to convert 1 g of the polymer (or crystal) into 1 g of the individual repeating units, J-g^{-1}

E activation energy for thermal degradation, J-mole^{-1}

FSV statistical mean fragment size vaporizing, dimensionless

$FSSL$ statistical mean fragment size at the solid-liquid interface, dimensionless

k coefficient of thermal conductivity, J-cm^{-1}-s^{-1}-°C^{-1}

L thickness of the surface melt layer in composite propellant combustion, cm

ℓ thickness of the surface melt layer in the self-deflagration of AP single crystals, cm

$\mathcal{M}$ molecular weight, g • (g-mole)$^{-1}$

$\dot{m}'''$ gas phase combustion rate during uniform combustion, g-cm^{-3}-s^{-1}

N fractional number of backbone bonds referred to the number in the undegraded state, dimensionless

n empirical index of pressure in the steady burning rate law for propellants, dimensionless

P pressure, N/m^2

R_i constants (with $i = 1, 2, 3, \cdots$) used for shorthand notations, dimensionless

$\mathscr{R}$ universal gas constant, J-mole^{-1}-°C^{-1}

$\mathscr{R}$ complex (pressure) response function, dimensionless

r linear regression rate, cm-s^{-1}

T temperature, K

t time coordinate, s

u gas (mass flow) velocity above the burning propellant, cm-s^{-1}

v volume fraction of oxidizer in a composite propellant, dimensionless

X, x distance coordinate, cm

x^* flame standoff distance, cm

α empirical constant in the *FSV* rule, (N/m^2)$^\beta$

β empirical index of pressure in the *FSV* rule, dimensionless

δ empirical constant in the *FSV* equation, K^{-1}

ϵ a small parameter used in the expansions; any first order quantity; $r'/\bar{r}$, dimensionless

ζ normalized flame standoff distance, dimensionless

θ_a activation energy parameter, $\equiv E/\mathscr{R}T_w$, dimensionless

κ thermal diffusivity, cm^2-s^{-1}

λ normalized time-independent regression rate eigenvalue, dimensionless

μ normalized amplitude of pressure fluctuations, dimensionless

ρ density, g-cm^{-3}

τ normalized temperature, dimensionless

ψ thickness of the surface melt layer on the oxidizer crystals in a composite propellant, cm

Ω normalized frequency of fluctuations, $\equiv \omega\kappa/\bar{r}^2$, dimensionless

ω frequency of fluctuations, s^{-1}

Subscripts and superscripts

$( )_b$ plane of burning, i.e., flame zone

$( )_0$ deep solid (ambient) conditions

$( )_{sL}$ solid-liquid interface plane

$( )_w$ wall plane

$\bar{( )}$ time-averaged part

$( )'$ fluctuating part

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